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Polypyrrole Stability and Coatings for Radar Absorbing Materials

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Defence R&D Canada – Atlantic

Technical Memorandum
DRDC Atlantic TM 2004-299
December 2004

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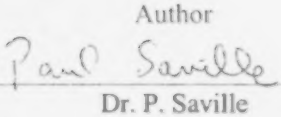

Dr. P. Saville

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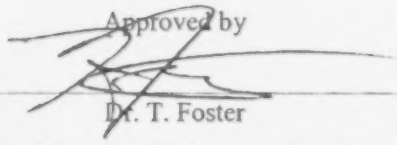

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Abstract

Resistive materials absorb microwaves by converting the induced current into heat. Polypyrrole is an electrically conducting polymer that has the potential to be used as a radar absorbing material. The long-term electrical stability of polypyrrole and its composites will determine its utility for advanced applications. This paper describes the formulation of coating materials containing polypyrrole synthesized with different counter ions. Observations of the electrical and permittivity stability of the powders and coatings are presented as a function of time. The results show that embedding the conductive material in a matrix stabilises the properties. The results also highlight the challenges that will be faced in reproducibly formulating a coating with consistent properties.

Résumé

Les matériaux résistifs absorbent les micro-ondes en transformant le courant induit en chaleur. Le polypyrrole est un polymère électro-conducteur qui pourrait être utilisé comme matériau absorbant les ondes radar. L'utilité du polypyrrole et de ses composites dans des applications de pointe dépendra de la stabilité électrique à long terme de ces matériaux. Dans cet article, on décrit la préparation de matériaux de revêtement contenant du polypyrrole synthétisé en présence de différents contre-ions. La stabilité électrique et la constance de la permittivité des poudres et des revêtements sont présentées en fonction du temps. Les résultats obtenus indiquent que le noyage du matériau conducteur dans une matrice permet de stabiliser les propriétés. Ces résultats donnent également un aperçu des défis qu'il faudra relever pour préparer systématiquement un revêtement présentant toujours les mêmes propriétés.

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Executive summary

Introduction

Optimised radar absorbing materials require specific properties (thickness, conductivity, permittivity and permeability) that cannot change with time without degrading the absorber's performance. Absorbers made from organic materials such as conducting polymers are lightweight and have properties that can be tuned through synthesis and processing. A concern for organic materials is oxidation or other degradation processes that will compromise their properties. In this paper, chemistry and coating formulation factors are studied for the conducting polymer polypyrrole.

Results

Synthetic variables that affect polypyrrole's conductivity include counter ion, counter ion ratio to monomer, particle processing and material density. Coatings formulated from polypyrrole powders are affected by the powder characteristics, mixing and weight percent polymer in the final coating. Exposure of these materials to oxygen results in their degradation with the rate being accelerated at elevated temperatures. Encapsulation of the conducting material in a coating matrix reduces the degradation process.

Significance

These results show that it is possible to formulate polypyrrole into a coating, making it more stable to oxidation and aging. This makes it viable for use in radar absorbing materials.

Future plans

Reproducible production of a coating with specific properties needs to be achieved. The development of coating materials with a wider range of permittivities also needs to be explored.

Leslie, A.; Kopac, M.; Saville, P.. 2004. Polypyrrole Stability and Coatings for Radar Absorbing Materials. DRDC Atlantic TM 2004-299. Defence R&D Canada – Atlantic.

Sommaire

Introduction

Pour présenter des caractéristiques optimales, les matériaux absorbant les ondes radar doivent posséder des propriétés bien précises (épaisseur, conductivité, permittivité et perméabilité) qui ne changeront pas avec le temps sans diminuer le rendement de l'absorbeur. Les absorbeurs faits de matériaux organiques tels que des polymères conducteurs sont légers et présentent des propriétés qu'il est possible de régler lors de la synthèse et du traitement. L'oxydation et d'autres processus de dégradation risquent de nuire aux propriétés des matériaux organiques. Dans cet article, on examine la chimie du polypyrrole électro-conducteur et les facteurs relatifs à la préparation de revêtements faits à partir de ce matériau.

Résultats

Parmi les variables de synthèse qui influent sur la conductivité du polypyrrole, on compte le contre-ion, le rapport contre-ion/monomère, le traitement des particules et la densité du matériau. Les revêtements préparés à partir de poudres de polypyrrole dépendent des caractéristiques des poudres utilisées, du processus de mélange et de la teneur massique en polymère du revêtement final. Exposés à de l'oxygène, ces matériaux se dégradent à un taux qui augmente avec la température. On peut réduire ce taux de dégradation en encapsulant le matériau conducteur dans une matrice.

Portée

Selon ces résultats, il est possible de préparer un revêtement fait de polypyrrole qui résiste à l'oxydation et au vieillissement et qui est alors utilisable comme matériau absorbant les ondes radar.

Recherches futures

Il faudra réussir à préparer systématiquement un revêtement présentant des propriétés bien précises. Il faudra également mettre au point des revêtements présentant une plus grande plage de permittivités.

Leslie, A.; Kopac, M.; Saville, P.. 2004. Polypyrrole Stability and Coatings for Radar Absorbing Materials. DRDC Atlantic TM 2004-299. Defence R&D Canada – Atlantic.

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1. Introduction

The materials used for microwave absorption can be classified as magnetic or electric materials. Magnetic materials are typically ferrites or carbonyl iron, while electric materials conduct currents induced by the electromagnetic waves. The resistance of the conductor converts the electrical energy into heat. Materials that have been used in microwave absorbers include carbon,[1,2] metal powders,[3] and conducting polymers.[4-7]

Conducting polymers are attractive materials for use as microwave absorbers due to their ability to be tuned with different properties based on synthetic control. These materials are also attractive due to their lightweight compared to magnetic materials. The ability of a conducting polymer to conduct electrical current lies in the polymer's conjugated π-system, which allows the polymer to act as a small band-gap semiconductor. An oxidised polymer such as polypyrrole, stabilised by an anionic counter ion or "dopant", can have high conductivities.[8]

The extended π-conjugation of polypyrrole that makes it conductive, also makes the polymer difficult to process into useful forms. Oxidative synthesis of polypyrrole produces an intractable powder, which is insoluble in all common solvents. Novel processing techniques such as polymerising the polymer directly on fabrics[9-13] and dispersions[13] in suitable matrices have been investigated to improve this shortcoming.

The conductivity of polypyrrole is not stable and decreases with time. The degradation rate is influenced by: temperature, oxygen level and dopant species. Thermal stability experiments, have shown that the rate of conductivity degradation increases with increasing temperature[14,15]. The process follows kinetics characterized by a diffusion-controlled mechanism at high temperatures and first-order kinetics at lower temperature[16]. It is thought that the conductivity loss is due to the diffusion of oxygen into the polymer[14] where it can react to form functional groups such as carbonyls that disrupt the conjugated π-network. It has also been proposed[17] that the conductivity loss is due to a process in which oxygen exchanges with the dopant species, and subsequently oxidises the polymer backbone. The aging of polypyrrole samples at elevated temperatures under inert atmospheres such as argon and nitrogen[15,18] does not affect conductivity even when the temperature is raised to 200°C. Dopants also affect the rate of conductivity decrease. Aryl sulfonates have been shown to slow this loss compared to mineral anions. It is thought that the aryl sulfonates are less susceptible to volatilization, decomposition and chemical reaction[17].

In this study, experimental conditions such as dopant, temperature and matrix are examined to investigate their affect on the electrical stability of the polypyrrole polymer and to develop methods of incorporating it into coating systems. Polymer stability is monitored by conductivity and permittivity measurements.

2. Experimental

2.1 Synthesis of Conducting Polypyrrole Powder

Chemically synthesized polypyrrole was used for all experiments. This was synthesized by using an oxidation method. In this case, ferric chloride hexahydrate (21.6 mmol), $FeCl_3$, was used as the oxidant. The method used for the synthesis was as follows: $FeCl_3$ was added along with a dopant (2.3 mmol) (in the case of these experiments dopants were aryl-sulphonates, Table 1) to 750 mL of high purity H_2O, 0.75 mL of conc. HCl and 1 mL of distilled pyrrole (7.2 mmol) were then added. The reaction vessel was then placed in an environmental chamber set at 1°C were it was mechanically stirred and allowed to polymerize for 24 hours. The ratio of oxidant to monomer was set to 3:1. After the 24 hour polymerization period, the reaction vessel was removed and the black opaque liquid was suction filtered leaving black polypyrrole powder. This powder was then dried under vacuum for 12 hours.

Table 1. Dopants and Acronym

DOPANT	ACRONYM
Anthraquinone-2-sulfonic acid, sodium salt	AQSA
Anthraquinone-2,6-disulfonic acid, disodium salt	AQDSA
1-Naphthalene sulfonic acid, sodium salt	NSA-1
2-Naphthalene sulfonic acid, sodium salt	NSA-2
1,5-Naphthalenedisulfonic acid, disodium salt	NDSA
Para-toluene sulfonic acid	PTSA

2.2 Formation of Polypyrrole Coated Fabric

Polypyrrole coated fabrics were made in the same manner as the powder above except for the inclusion of a piece of poly(ethylene terephthalate) (PET) to the reaction vessels. The reaction vessels were then placed on a rotating platform and slowly rotated at 1°C for 24 hours. The pieces were then removed and washed with distilled water to remove any loosely adhering polymer. A 2.54 cm by 5.08 cm rectangle was then cut out of the fabric. This rectangle of polypyrrole coated PET was then used to make conductivity measurements.

2.3 Polypyrrole Pellet Formation

Pellets of polypyrrole/dopant were made by measuring approximately 150 mg of ppy powder into a 13 mm die press compressed to 138 MPa (10 tons/in^2) for a period of 2 minutes. The pellets produced were thin black cylinders with a uniform appearance.

2.4 Coating Formulation

Several commercial coating systems were used for the formulation of polypyrrole coatings. The products used were

a. Latex: A carboxylated styrene/butadiene latex dispersed in water from Dow Chemical Inc (Dl 238Na), the latex was found to contain 43.5% volatiles.

b. Alkyd#1: A Sico epoxyflex modified alkyd. With the epoxyflex systems varsol had to be added to achieve paints over 15% ppy to allow application by conventional means. This coating has a low pigment content so higher loadings of PPy could be achieved.

c. Alkyd#2: A marine enamel alkyd paint containing 30% volatiles from Cloverdale Paint.

d. Alkyd#3: A urethane modified alkyd marine trim enamel with 15.1% volatiles.

e. Polyurethane (GP-200): A two part urethane/talc non-slip coating. The GP-200 is a very viscous paint to begin with so in most cases above 7% ppy had to be applied with a troweling technique. The curing times between the two systems varied as epoxyflex > GP-200.

f. Epoxy: A two-part epoxy paint system from International Paints Ltd., consisting of base coat and curing agent. The parts were mixed in a 4:1 ratio by volume of base coat to curing agent. The base coat was a low molecular weight epoxy resin dispersed in xylene and n-butanol. The curing agent contained polyamino amide and propylene glycol methyl ether with a xylene continuous phase. The base coat and curing agent were found to be 44.2 and 58.9 % volatiles.

Initial attempts to incorporate polypyrrole into paint systems yielded very rough films even after grinding through implementation of a mortar and pestle. Ball milling helped but measurable conductivities were illusive with these preps. The bulk powders were sifted through a 590 micron screen before subsequent paint mixtures were formulated. This achieved a smoother finish as well as bulk to the paint without a loss of measurable conductivity. A speed mixer (Flactec) was used to mix polypyrrole into the GP-200 base (1 5 minutes @ 2400 rpm).

2.5 Conductivity Measurements

The conductivity of the 13mm diameter polypyrrole pellets, fabric and paints were determined using a Jandel multi-height four-point probe apparatus. D.C conductivity measurements for paint samples were also made using small polyacrylic plaques, which had a conducting silver paint covering the ends of one face. Thin wires were embedded into the epoxy and the sample would be painted onto the plaque covering one side. A voltmeter attached to the wires was used to measure resistance. IR measurements on pellets were made using a Nicolet Nexus 670 FT-IR spectrometer with a Thunderdome attachment. Pyrolysis data was gathered with the Nexus 670 equipped with a Pyroprobe 2000 attachment. Thermal measurements were made using a TGA 51 and a DSC 910. Both the thermogravimetric analyzer and the differential scanning calorimeter were made by TA instruments. For DSC and TGA runs a heating rate of 10°C/min. was used unless otherwise stated.

2.6 Permittivity Measurements

Samples were machined to fit closely into an X-band waveguide and the S-parameters measured with either a HP 8720C or an Agilent 8364B vector network analyser. The permittivity was fit to the experimental S-parameters by calculating S-parameters based on the material structure and permittivity. The permittivity was varied by a nonlinear least squares optimisation routine that minimised the difference between the experimental and calculated S-parameters.

2.7 Weathering

Weathering of paint samples was done using ASTM method D 5894. Ultra-violet/Condensation exposure was done using an Atlas screening device. Fog exposure was done using a Prohesion fog cabinet.

3. Results

3.1 Polypyrrole Coated Fabric

Polypyrrole can be coated onto fabrics by immersing a fabric in a solution containing the reactants for polymerisation of polypyrrole. A uniform coating of polypyrrole is deposited on the fabric with the polymer forming a shell around the individual fibres of the material. The conductivity of the material can be varied over a wide range by controlling deposition time, reagent concentrations, temperature and dopant ions. Here, the amount of HCl included in the synthesis was varied to determine if there was a correlation between the conductivity stability over time and the amount of acid added. Experimental conditions were set with acid volumes varying from 0 to 0.04 mL. All other experimental conditions were kept constant. The experiment is summarized in Table 1.

The samples were aged at room temperature in an open atmosphere and the conductivity measured throughout a 2.5 week period. In the plot of normalized conductivity vs. time (Figure 1 bottom), each sample showed an initial increase in conductivity over the first 24 hours. After this period the conductivity decreased at a constant rate until the end of the experiment. By the 20th day the conductivities had decreased at least to their initial values for each sample. Over the next 75 day period the loss of conductivity tapered off. The rates of decay are similar for all samples with a value of approximately -0.005 Scm^{-1}/day for the first 20 days and –0.001 Scm^{-1}/day for the last 75 days. From the limited experimental results the most stable material appears to have been made with the 0.02 mL of added acid. Further experimentation needs to be carried out to confirm this observation and to determine if there are any correlations to be drawn.

Table 2. Summary of Fabric Aging

AMT. OF ACID ADDED (mL)	INITIAL CONDUCTIVITY (S/cm)	RATE OF CHANGE IN CONDUCTIVITY AFTER INITIAL INCREASE (Scm^{-1}/DAY)
0	0.566 ± 0.008	-0.0011
0.01	0.775 ± 0.005	-0.0011
0.02	0.678 ± 0.005	-0.0003
0.03	0.837 ± 0.006	-0.0010
0.04	0.68 ± 0.02	-0.0006

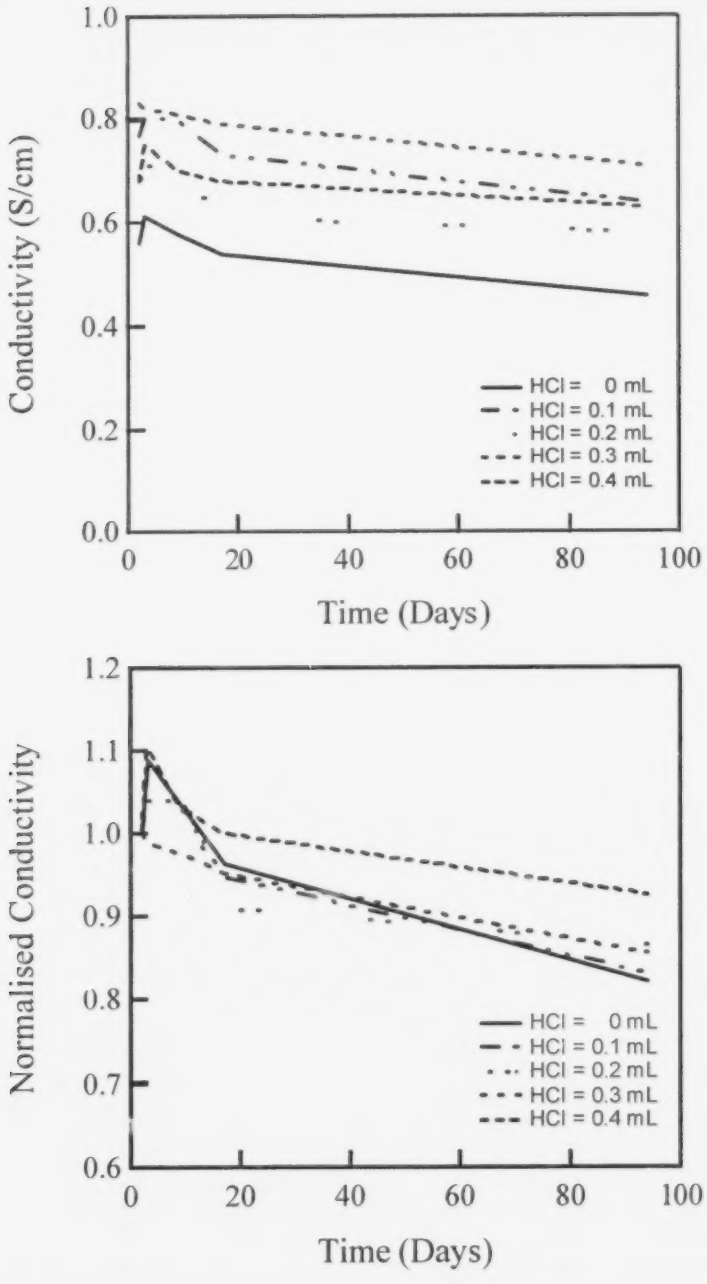

Figure 1. Conductivity top and normalised conductivity ($\sigma/\sigma_{initial}$) bottom as a function of aging time.

3.2 Polypyrrole Pellets

Pellets formed by compressing polypyrrole powder were also used for studying aging effects. Several factors were noted to have an affect on pellet conductivity and these are considered as well.

3.2.1 Effect of Pellet Density

A variation was noted in the conductivity of pellets pressed from the same batch of polypyrrole. To understand this observation the density of the pellets were determined, and the conductivity ploted as a function of the density, Figure 2. Essentially this plot is a straight line up to a density of about 1.16 g/cm^3, after which the conductivity appears to plateau.

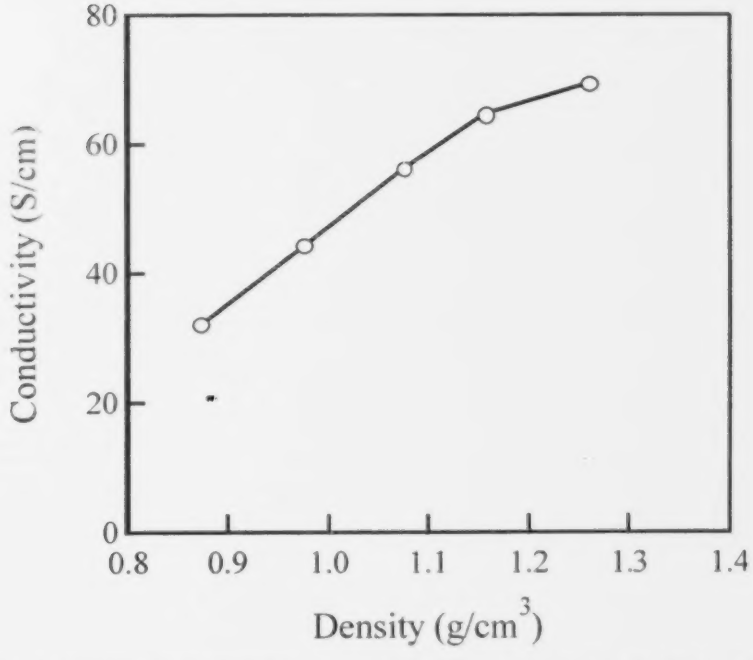

Figure 2. *Conductivity of pressed polypyrrole pellets as a function of pellet density. Dopant is NSA-1.*

3.2.2 Effect of Powder Milling

Two different milling techniques were used to make a fine powder of an AQDSA doped PPY. Some of the powder was ground with a mortar and pestle for 10 minutes, some was ground in a ball-mill for 30 minutes and some was un-milled as a control. Pellets were pressed from these powders and the measured conductivities plotted in Figure 3. At first appearance the order of increasing conductivity is ball-milled < un-milled < mortar and pestle (Top Figure 3). Examination under a microscope at 50.69X magnification showed a difference between the powders. Ball milling produced the smallest particle size followed by the mortar and pestle then the non-processed.

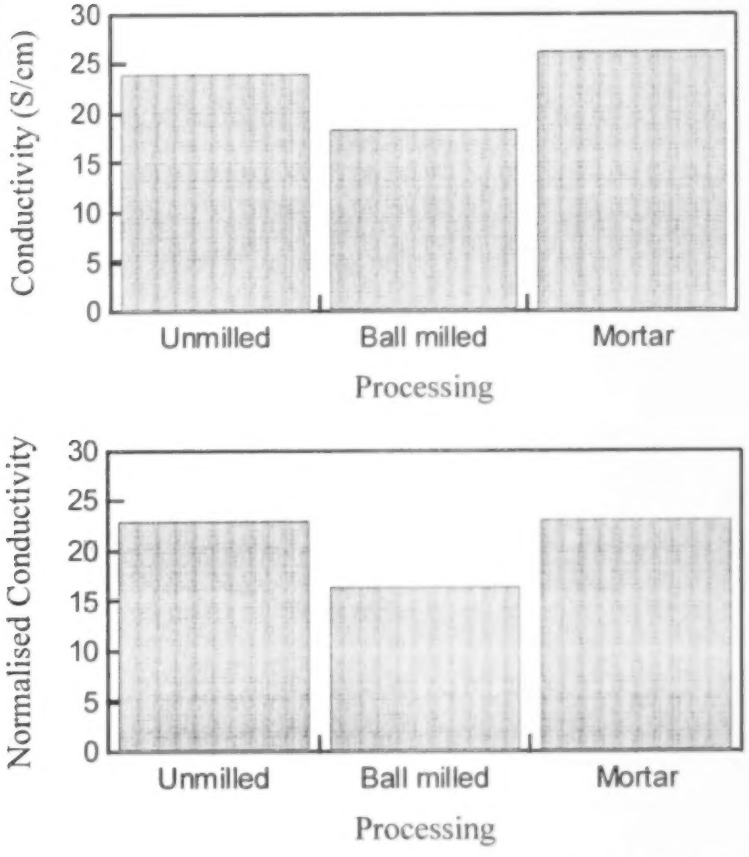

Figure 3. *Top, conductivity of polypyrrole pellets pressed from powders milled in different ways. Bottom, same plots with the conductivity normalised by the density. Dopant used AQDSA.*

In light of the effect of density on the conductivity, the conductivity of these three pellets were normalised by dividing by the pellet density. The result is that the normalised conductivities of the un-milled and mortared pellets are the same, while the ball milled powder produced the pellet with the lowest conductivity. These results indicate that excessive grinding or ball milling degrades the polypyrrole conductivity.

3.2.3 Effect of Dopant on Pellet Conductivity

PPy powders were prepared with the dopants listed in Table 1. Each polymer was prepared in the same manner and resulted in indistinguishable fine black particles regardless of the dopant. Pellets were pressed for the different powders and the conductivity measured (Figure 4).

Measured conductivities ranged from about 10 to 40 S/cm, with the disulfonic acid salts yielding the highest conductivity and AQSA the lowest. This trend partially agrees with other findings,[14] however, the density of the pellets were not taken into account. Pellets made with AQSA, PTSA and $FeCl_3$ doped polypyrrole had the lowest densities while AQDSA, NDSA and NSA typically had high densities. At this time is not known if this density trend is inherent in the chemical nature of the material or the way in which the powders were compressed into pellets. AQDSA and NDSA doped polypyrrole pellets have similar normalised conductivities, as do PTSA, NSA and $FeCl_3$. AQSA has a lower normalised conductivity. Note the comparison of normalised conductivity may not be valid for differently doped polypyrroles.

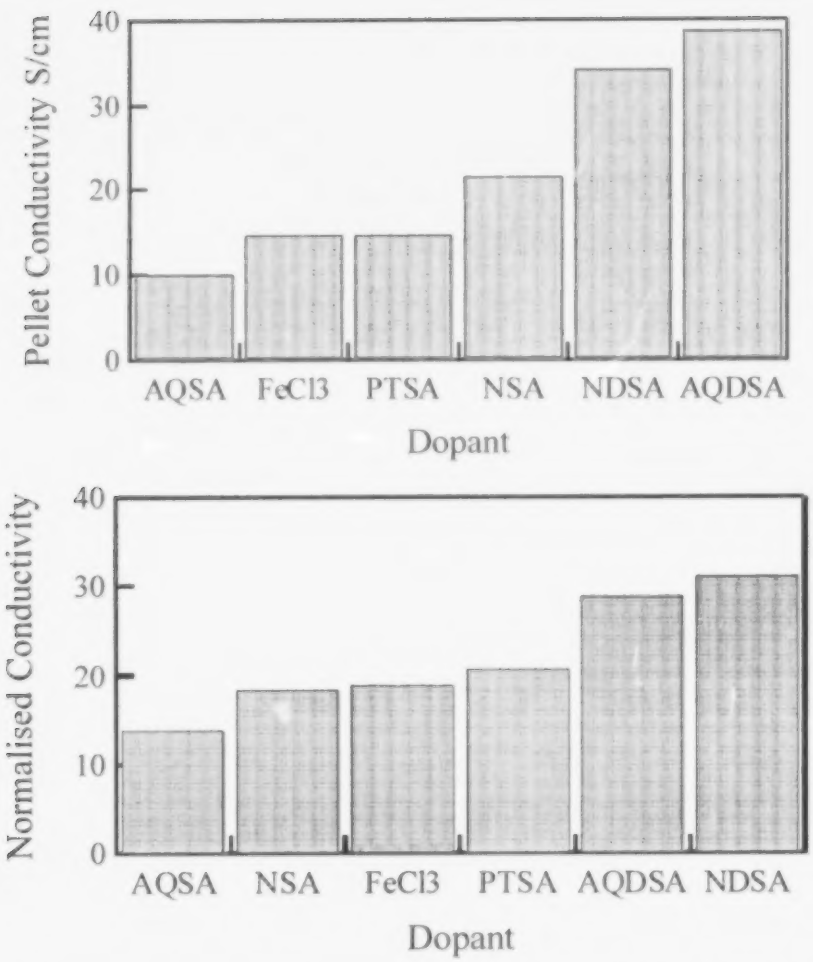

Figure 4. *Top, conductivity of pressed polypyrrole pellets as a function of dopant. Bottom, normalised conductivity (conductivity/density) of the same pellets.*

3.2.4 Effect of Dopant to Monomer Concentration Ratio

The data shown in Figure 5 indicate that the conductivity approaches a maximum as the ratio of dopant to monomer approaches 1:3. This ratio is typical for the number of dopant ions to pyrrole rings in oxidised polypyrrole. The scatter in data at this ratio likely arises from concentration variations in the actual reaction mixture.

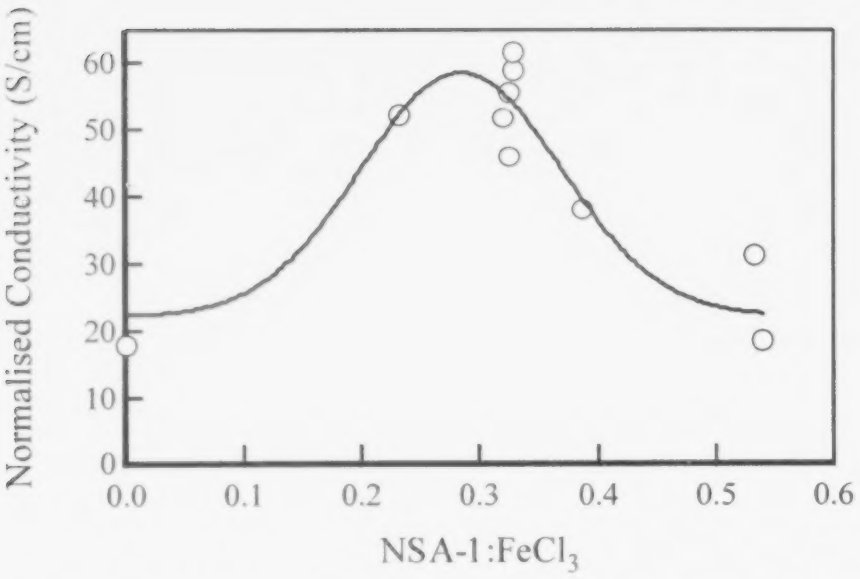

Figure 5. *Effect of dopant to monomer ratio on the conductivity (normalised for density) of pressed polypyrrole pellets. Dopant ion NSA-1.*

3.2.5 Effect of Aging and Temperature on Pellet Conductivity

Four groups of three ppy pellets were prepared with each group having a different dopant. Dopants used were NDSA, NSA, AQDSA and PTSA. Each of the three pellets from the groups were aged in different temperature environments. These environments were in an oven set to 85 °C, a freezer set to –18 °C and at room temperature. Conductivity measurements were then made on the pellets over the course of a 2.5 week period, Figures 6-8. Both the low and room temperature pellets showed linear character in the conductivity vs. time plot with the room temperature pellets degrading slightly and the low temperature pellets being essentially stable throughout the test period. The NSA pellets did not follow this linear pattern. These pellets gave an erratic progression, which very roughly followed the same trends as the other PPy/dopant pellets. After the initial 20 day period, the rate of conductivity loss decreased. After the 20 day period the conductivity for PPy/PTSA appears to have increased.

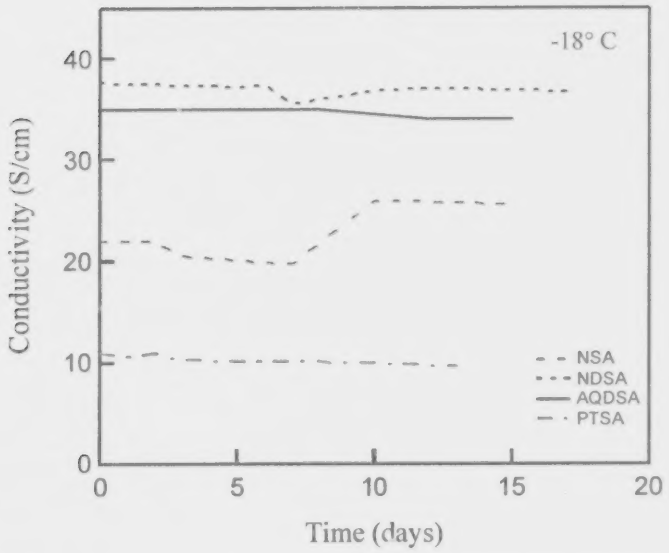

Figure 6. *Decrease in conductivity as a function of time for polypyrrole doped with different ions at -18° C.*

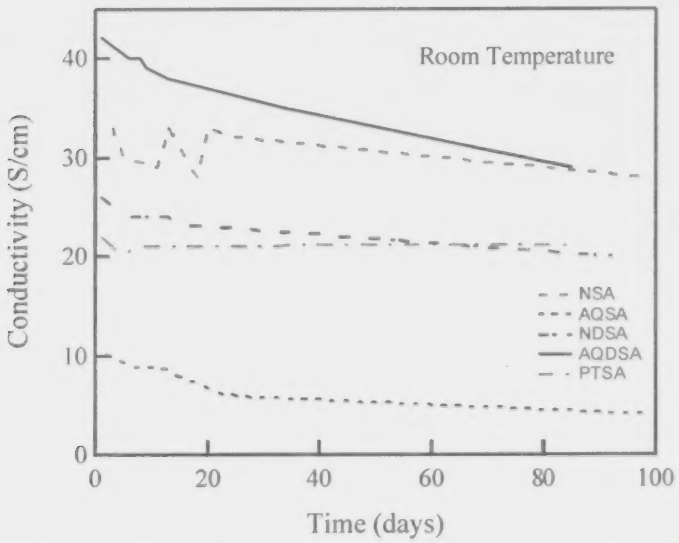

Figure 7. *Room temperature decrease in conductivity as a function of time for polypyrrole doped with different ions.*

The pellets exposed to the higher temperature did not follow a linear relationship with time, Figure 8. The normalized conductance vs. time plot showed a rapid decrease in conductivity over the initial six day period and from that point decreased less rapidly. Following the work of Truong[18], a plot of $\Delta\sigma/\sigma_o$ vs. $t^{1/2}$ (with $\Delta\sigma = \sigma_o - \sigma_t$) was found to be linear up to $\Delta\sigma/\sigma_o = 0.5$. Troung compares this plot to the Fickian sorption plot of M_t/M_∞ vs. $t^{1/2}$ where M_t is the absorbed mass at time t and M_∞ is the equilibrium absorbed mass. Assuming that the decrease in conductance is proportional to the amount of absorbed oxygen and that the initial conductance is much greater than the conductance at time t, Troung states that $\Delta\sigma/\sigma_o$ is proportional to M_t/M_∞ meaning that, at least up to $\Delta\sigma/\sigma_o = 0.5$, the degradation follows Fickian sorption kinetics. Diffusion coefficients were calculated using the following equation: $D = 0.04939l^2/t_{0.5}$ with l= thickness of the film and $t_{0.5}$ = time at which $\Delta\sigma/\sigma_o = 0.5$. Calculated diffusion coefficients are seen in table 2.

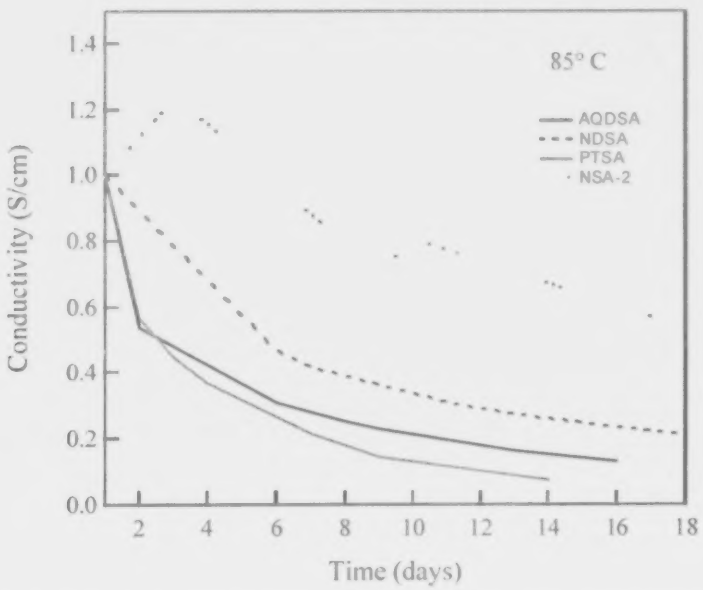

Figure 8. *Decrease in normalised conductivity as a function of time for polypyrrole doped with different ions at 85° C*

As was the case at low and room temperature, NSA-2 gave erratic conductivity measurements and therefore a diffusion coefficient was not calculated. From the plot of normalized conductance vs. time and the calculated diffusion coefficients the order of increasing rate of loss of conductance at 85° C is: NSA-2 < NDSA < AQDSA < PTSA.

Table 3. Diffusion coefficients calculated from loss of conductivity of polypyrrole pellets doped with different ions.

DOPANT	CONDUCTIVITY (S/cm)	DIFFUSION COEFFICIENT (CM^2/s)
AQSA	9.7 ± 0.2	-
NDSA	23 ± 4	5.73×10^{-10}
NSA-2	33 ± 5	-
PTSA	21 ± 1	1.68×10^{-09}
AQDSA	41 ± 6	7.13×10^{-10}

3.2.6 IR Study of Polypyrrole Pellets

Three pellets were made from a single batch of PPy/AQDSA powder and aged at –18 °C, room temperature and 85 °C for a period of two weeks. After the two week period the IR reflectance spectra for each was collected. From these spectra, the intensity of the peaks at 1500 cm^{-1} were compared to determine if there was correlation between peak intensity at 1500 cm^{-1} and rate of conductance degradation. This experiment follows the work of Kaynak *et al.*[19] who monitored the peak intensity for samples aged at room temperature. Kaynak observed a slight increase in the intensity of the peak at 1690 cm^{-1} which was attributed to oxidation at the β' position on the pyrrole ring. The spectra collected (Figure 9) for this study, however, did not show such a relationship. The expected progression was an increase in absorption from low to high temperature. The peaks at 1590 cm^{-1} increased in absorption in the following order: room temp. < -18 °C < 85 °C, which does not reflect prior findings. This may be due to pellet density which was not accounted for.

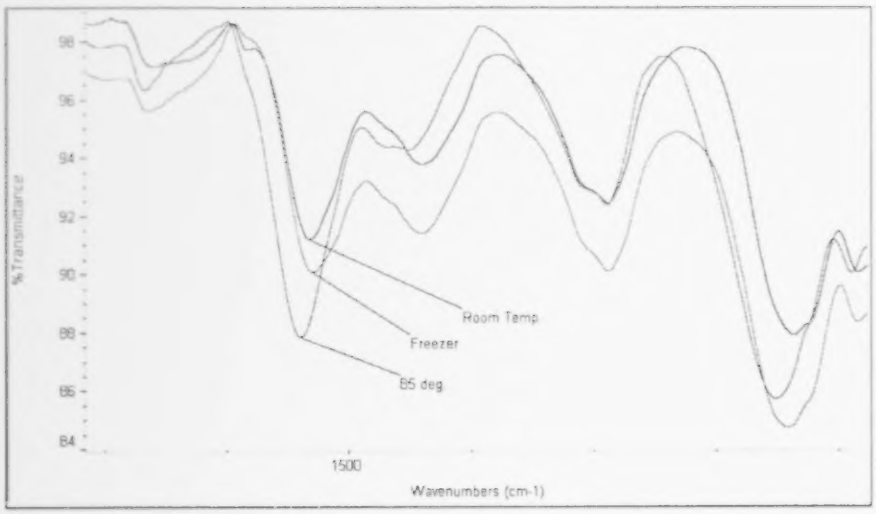

Figure 9. *Spectra for Three Temperatures*

Infrared pyrolysis spectra were collected from a sample of PPy/AQDSA. Six spectra were collected from the same sample in an increasing temperature range of 200, 300, 400, 500, 600 and 700 °C. There were no emissions of note from 200 to 500 °C. At 600 °C there were peaks characteristic of SO_2 at 1100 cm^{-1} and therefore the breakdown of the dopant. At 700 °C there were three groups of peaks: 3200, 2100 and 1100 cm^{-1}, which are typical of HCN, carbonyl sulphide and SO_2 respectively; breakdown products of the polypyrrole and dopant.

3.2.7 Thermal Analysis of Polypyrrole Powders

Thermogravimetric analysis, TGA, and Differential scanning calorimetry, DSC, information was obtained on PPy/AQDSA in epoxy paint at 3 and 5 weight percentage as well as on pure PPy powders with various dopants. These dopants were NSA-2, NDSA, PTSA and AQDSA. The TGA obtained from PPy/AQDSA powder showed three weight losses before 230° C. These weight losses occurred at 127, 160 and 215° C. Pyrolysis spectra were gathered at these temperatures and the 127 °C and 215° C weight losses were attributed to water and NO_2 respectively. TGA data of 3 and 5 weight percent PPy/AQDSA in epoxy showed a mass loss at 400 °C. This mass loss at 400° C was also observed for pure epoxy. DSC data of PPy powder with various dopants was obtained. The powder was initially heated at a rate of 20 °C/min. to 110° C to eliminate water. The sample was then cooled to room temperature and then heated at 10° C/min. to 250° C. Each sample showed a dehydration endotherm on the initial run. This endotherm was not observed after cooling and reheating. After the initial run, all dopants showed a single endotherm in the heating range. PPy/NDSA,

PPy/PTSA and PPy/AQDSA showed a broad endotherm centered around 130, 130 and 122°C respectively. PPy/NSA-2, however, displayed a narrow endotherm at 105°C.

3.3 Polypyrrole Coatings

Methods were developed to incorporate PPy powder as a dispersion into paint systems. Variables investigated were: Milling technique and time, painting technique and effects of weathering. The criteria used to judge the suitability of the paints after the addition of PPy were: quality of dispersion /coating and conductance.

3.3.1 Polypyrrole Powder Milling and Particle Dispersion

Powders from two different milling techniques (mortar and pestle and ball-milling) were compared to coatings made from un-milled powder (remember Figure 3). When these powders were mixed into the latex paint system the milled powders produced superior dispersions compared to the non-milled powder, with no visible discrete PPy particles. No significant differences were observed between the mortar and pestle and ball-mill powder dispersions in terms of coating appearance.

Several methods have been evaluated for dispersing the polypyrrole powder in the coating. These included hand mixing the powder with a stirring rod, a rotating platform, a ball-mill and a speed mixer from Flactec.

Powders ground in a mortar were added to the latex paint. Un-milled powder was used as a control. A suitable dispersion was produced with the ball-mill in approximately 30 seconds, compared to several hours for the rotary platform. The un-milled powder failed to form a suitable suspension by either method, illustrating the need for powder milling.

Addition of 10% (w/w) PPy powder to alkyd#2 produced a spongy material upon mixing. At this loading the critical pigment volume concentration was probably exceeded. Adding up to 2% varsol by volume increased the ability of the paint to incorporate the powder. When more than 2% thinner was added the coating was very "watery" and formed beads when applied to a surface surface. Thinner was also needed for the latex mixtures where water was used as the thinner. Thinning was unnecessary for the epoxy, Alkyd#1 and Polyurethane systems.

3.3.2 DC Conductivity of Polypyrrole Coatings

The conductivities of coatings, formulated with different weight percentage polypyrrole powder, are shown in Figure 10. The powder used for a series of coatings came from the same synthetic batch and were mixed into the alkyd#1 base with a stirring rod. At high loadings all of the formulations have approximately the same

conductivity. The series of coatings represented by the black line come from a batch of polypyrrole powder where a pressed pellet of the powder had a conductivity of 31 S/cm. This series required loadings of nearly 20 wt% polypyrrole before high conductivities were obtained. The transition point between low and high conductivities is often referred to as the percolation threshold. The percolation threshold for fine spherical particles has been theoretically calculated to be about 19 %, and the powder used for this series had been sieved through a finer screen that the other series. The other three series represented by the blue, green and red lines in Figure 1 show much the same behaviour, however, the percolation threshold is achieved with loadings of about 8-10 wt%.

The series in Figure 10, indicate that particle size and shape are major factors affecting the coating conductivity. Other factors affecting the coating conductivity arise from the degree of mixing. Hand mixing with a stirring rod will produce conductivities that vary from coating to coating.

The latex and other alkyd systems produced similar results. These result are in agreement with Costa *et al.*[20] who found a percolation threshold of 12% for a PPy/polystyrene composite. No conductivity could be measured from composites made with the epoxy coating.

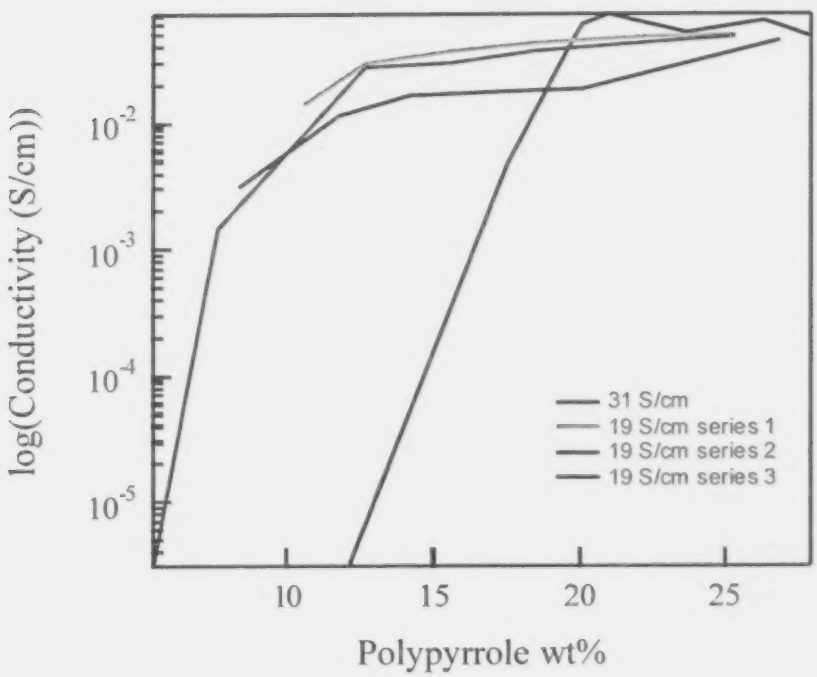

Figure 10. *Conductivity of some alkyd#1-polypyrrole coatings with the same formulation. Conductivity of pressed pellets of polypyrrole powder was 31 S/cm for black line and 19 S/cm for the other series.*

3.3.3 Permittivity of Polypyrrole Coatings

The real and imaginary components of the permittivity as a function of the weight percent polypyrrole for a series of polypyrrole coatings are shown in Figure 11. The logarithm of the permittivity has been plotted since there is a direct relationship between the imaginary permittivity and dc conductivity.

$$\varepsilon'' = -\frac{\sigma_{dc}}{\omega \varepsilon_o}$$

The percolation threshold is apparent in these parameters as well, occurring at about 8 wt% polypyrrole. After the percolation threshold the real and imaginary permittivity continue to slowly increase with higher PPy loadings.

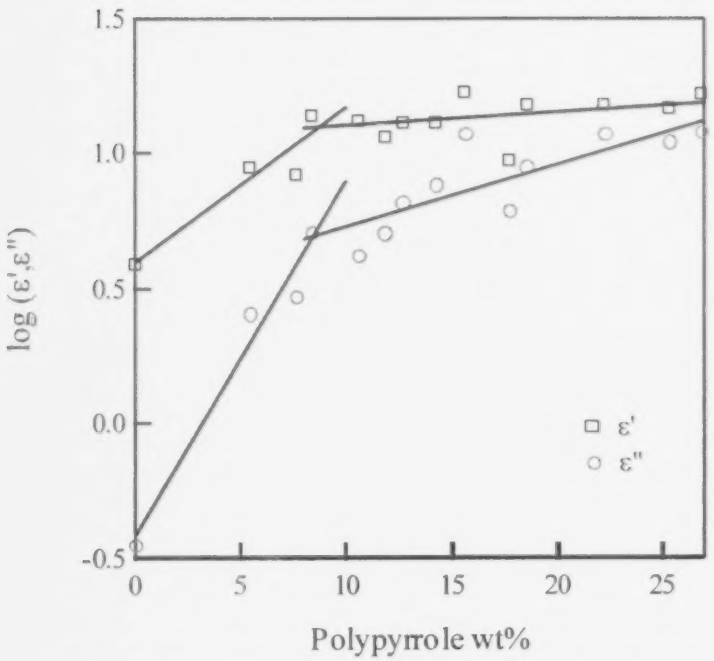

Figure 11. *Real and Imaginary components of the permittivity as a function of the wt% polypyrrole in alkyd#1 coating. All formulations originate from the same batch of polypyrrole made with NSA-1. ε', blue squares, ε'', red circles.*

The polyurethane coating was very thick even before incorporation of polypyrrole. The talc filler for this polyurethane coating was mixed in with the speed mixer and then the polypyrrole was blended in by hand or with the speed mixer. The permittivities of the resultant coatings are shown in Figure 12. Hand mixing produced a series of coatings with slightly higher real and imaginary permittivity. This is likely due to the speed mixer producing a more uniform distribution of the conducting particles in the matrix, which are then electrically isolated. The percolation threshold for this coating is low, at about 2.5 wt% PPy. This is likely due to the high viscosity of the coating and/or the talc surface facilitating the formation of conductive paths through the material.

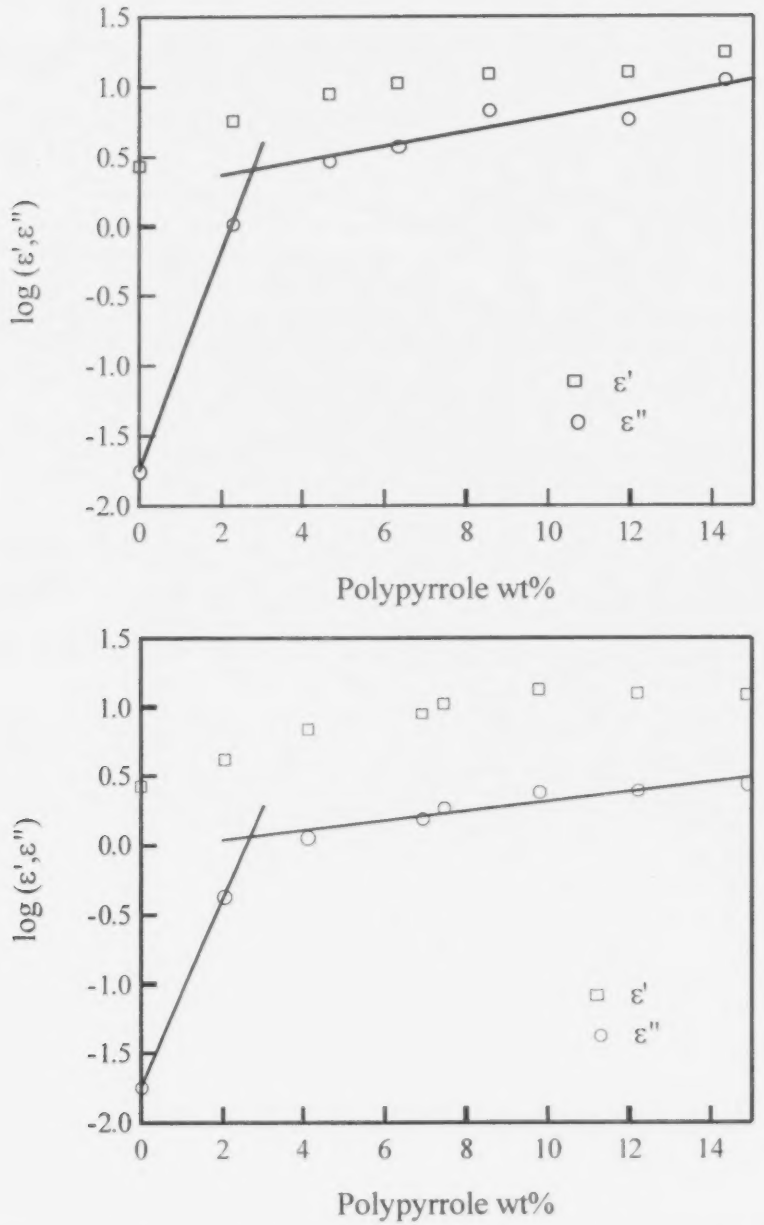

Figure 12. *Real and Imaginary components of the permittivity as a function of the wt% polypyrrole in the polyurethane non-skid coating. Top graph, hand mixed, bottom graph speed mixed. Dopant NSA-1.*

3.3.4 Weathering of Polypyrrole Coatings

Limited work has been done on weathering the coating materials. Paint samples were prepared and applied to rectangular polystyrene plaques. The samples consisted of alkyd#2 and epoxy mixtures. The powder used for each sample was PPy/AQDSA. The alkyd coatings were made up with three and five weight percent PPy. The epoxy samples contained one, three and five weight percent. The plaques were placed in the weathering cabinets for the 2 week cycle. Samples were collected from the plaques daily. After the 6th day the epoxies had become to0 brittle and sampling from these plaques was discontinued. Throughout the entire 2 week cycle the alkyd samples remained unaffected. Permittivity measurements were made on samples collected from the plaques prior to and during the weathering. These showed a fairly stable permittivity, Figure 13.

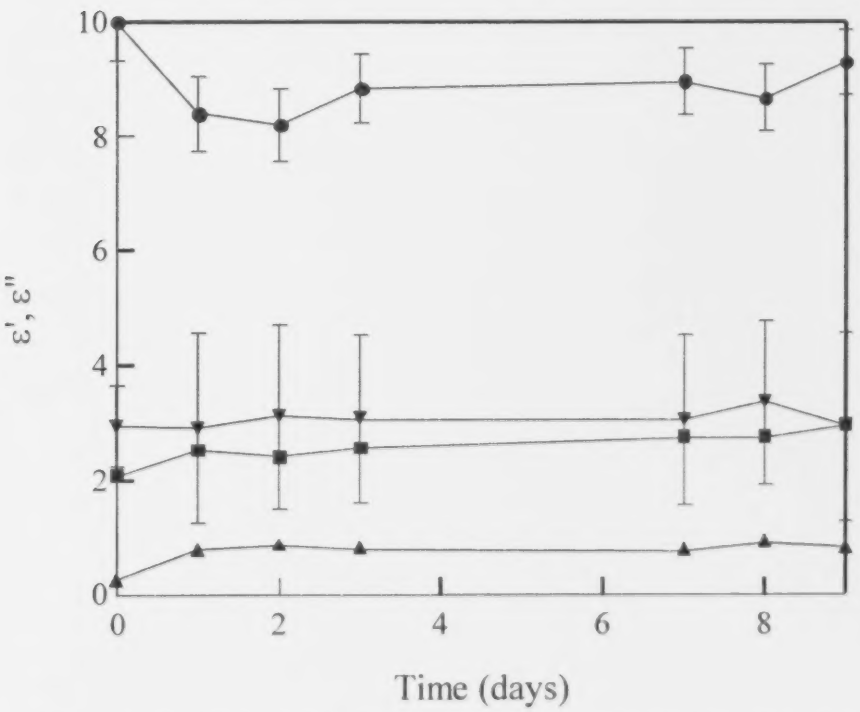

Figure 13. *Permittivity of PPy/AQDSA-Alkyd#2 coatings as a function of weathering time.*

4. Conclusions

Polypyrrole is inherently unstable to air oxidation. This was observed through the decrease in conductivity of the coated fabrics and pressed pellets. The oxidation rate is accelerated with increased temperature and decreased by limiting oxygen diffusion though encapsulation in a coating. Dopant ions affect the oxidation rate, possibly by forming different density polypyrrole/dopant particles. The higher density particles may exclude oxygen more effectively.

Density plays a large role in the conductivity of polypyrrole pellets (and potentially powders and coated fabrics as well). The density of a pellet needs to be taken into account when comparing different materials. Density differences may arise from the degree of compression during pellet formation, or they may arise from the presence of the dopant ions forming different density materials.

The amount of HCl present in the reaction does not appear to have a great influence on the oxidation rate of polypyrrole coated fabrics. Other work has shown that the dopant ion does have an effect on the oxidation rate of these materials, probably through the formation of dense polypyrrole layers.

For pellets pressed from polypyrrole powders, the dopant affects the conductivity. The disulfonates have a higher conductivity than do the monosulfonates, with AQSA having the lowest conductivity. This is in contrast to the results for polypyrrole coated fabrics where AQSA was found to form the highest conductivity and most stable material. Temperature experiments with PPy/dopant pellets showed that the electrical stability was inversely proportional to temperature. The data from the high temperature runs show similarities to the Fickian sorption plot up until $\Delta\sigma/\sigma o = 0.5$. This suggests that the conductivity loss is due to absorption of oxygen into the polymer. Calculated diffusion coefficients showed that at 85° C electrical stability follows the following order: NSA-2>NDSA>AQDSA>PTSA. IR spectra of aged PPy pellets were not conclusive possibly due to density effects. TGA data showed that PPy/AQDSA powder was not stable over 160° C. This should be taken into account when considering PPy for elevated temperature use. Further DSC experiments should be done to determine the nature of the endothermic peak present in each run of PPy/dopant powder.

For the coating systems, more work should be done to determine accurate percolation thresholds for each system. Milling the powder prior to mixing into the paint gave a better dispersion for each system. Also, mixing coating/powder with a ball-mill and immediate coating were found to give the best results. In each case the optimum coating was given by the following method:

Initially grinding powder with mortar& pestle.

Adding no more than 2% of appropriate thinner to paint.

Adding ground powder to paint.

Ball-milling to disperse the powder in the coating for at least 2 minutes

Painting coat immediately after mixing.

Not exceeding 130 μm thickness for each coat.

Weathering tests were preformed on alkyd and epoxy systems. Given that the epoxy system suffered severe degradation after only 6 days indicates that the epoxy is not suitable in its present form. The alkyd remained stable throughout the weathering period and shows promise as vehicle for radar absorbing coatings.

The utility of polypyrrole (or other conducting particles) coatings as radar absorbing materials requires high stability and reproducible formulation of the material properties. The results here indicate that the stability issue will be satisfied when the polypyrrole is encapsulated in a coating. Reproducible formulation will require tight control of synthetic conditions, milling (particle characteristics), and most importantly powder dispersion in the coating. High viscocity coatings and inclusions that affect the distribution of conducting particles may give better control over the coating properties.

It may be more expedient to formulate a coating from scratch rather than use a commercial product.

5. References

(1) Severin, H. *IRE Trans. Antennas & Propagat.* **1956**, *AP-4*, 385.

(2) Tanner, H. A., US Patent 2977591. **1961**.

(3) Janos, W. A., US Patent 5298903. **1994**.

(4) Mohamed, A. B. H.; Miane, J. L.; Zangar, H. *Polymer International* **2001**, *50*, 773.

(5) Gregory, R. V.; Kimbrell, W. C.; Kuhn, H. H. *Synth. Met.* **1989**, *28*, C823.

(6) Bjorklund, R. B.; Lundstroem, I. *J. Electron. Mat.* **1984**, *13*, 211.

(7) Vinoy, K. J.; Jha, R. M. *Radar Absorbing Materials: From theory to Design and Characterization*; Kluwer Academic Publishers: Boston, **1996**.

(8) Chandrasekhar, P. *Conducting Polymers, Fundamentals and Applications: A Practical Approach.*; Kluwer Academic Publishers: London, **1999**.

(9) Adams, L. W.; Gilpatrick, M. W.; Cuddihee, M. E., US Patent 5292573. **1994**.

(10) Buckley, L. J., Eashoo, M. *Synthetic Metals* **1996**, *78*, 1.

(11) Heisey, C. L.; Wightman, J. P.; Pittman, E. H.; Kuhn, H. H. *Textile Res. J.* **1993**, *63*, 247.

(12) Kuhn, H. H.; Kimbrell, W. C.; Worrell, G.; Chen, C. S. *Tech. Pap. Soc. Plast. Eng.* **1991**, *37*, 760.

(13) Truong, V.-T., Riddell, S. Z., Muscat, R. F. *J. Mat. Sci. Lett.* **1998**, *33*, 4971.

(14) Thieblemont, J. C.; Planche, M. F.; Petrescu, C.; Bouvier, J. M.; Bidan, G. *Polymer Degradation and Stability* **1994**, *43*, 293.

(15) Chen, X. B.; Issi, J.-P.; Devaux, J.; Billaud, D. *Journal of Materials Science* **1997**, *32*, 1515.

(16) Ennis, B. C.; Truong, V.-T. *Synthetic Metals* **1993**, *59*, 387.

(17) Thieblemont, J. C.; Planche, M. F.; Petrescu, C.; Bouvier, J. M.; Bidan, G. *Synthetic Metals* **1993**, *59*, 81.

(18) Truong, V.-T.; Ennis, B. C.; Turner, T. G.; Jenden, C. M. *Polymer International* **1992**, *27*, 187.

(19) Kaynak, A., Rintoul, L., George, G.A. *Materials Research Bulletin* **2000**, *35*, 813.

(20) Costa, L. C.; Henry, F.; Valente, M. A.; Mendiratta, S. K.; Sombra, A. S. *Eur. Polym. J.* **2002**, *38*, 1495.

List of symbols/abbreviations/acronyms/initialisms

DND	Department of National Defence
PPy	Polypyrrole
HCl	Hydrochloric acid
DSC	Differential Scanning Calorimeter
TGA	Thermogravimetric Analyser

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14. ABSTRACT

(U) Resistive materials absorb microwaves by converting the induced current into heat. Polypyrrole is an electrically conducting polymer that has the potential to be used as a radar absorbing material. The long-term electrical stability of polypyrrole and its composites will determine its utility for advanced applications. This paper describes the formulation of coating materials containing polypyrrole synthesized with different counter ions. Observations of the electrical and permittivity stability of the powders and coatings are presented as a function of time. The results show that embedding the conductive material in a matrix stabilises the properties. The results also highlight the challenges that will be faced in reproducibly formulating a coating with consistent properties.

(U) Les matériaux résistifs absorbent les micro-ondes en transformant le courant induit en chaleur. Le polypyrrole est un polymère électro-conducteur qui pourrait être utilisé comme matériau absorbant les ondes radar. L'utilité du polypyrrole et de ses composites dans des applications de pointe dépendra de la stabilité électrique à long terme de ces matériaux. Dans cet article, on décrit la préparation de matériaux de revêtement contenant du polypyrrole synthétisé en présence de différents contre-ions. La stabilité électrique et la constance de la permittivité des poudres et des revêtements sont présentées en fonction du temps. Les résultats obtenus indiquent que le noyage du matériau conducteur dans une matrice permet de stabiliser les propriétés. Ces résultats donnent également un aperçu des défis qu'il faudra relever pour préparer systématiquement un revêtement présentant toujours les mêmes propriétés.

15. KEYWORDS, DESCRIPTORS or IDENTIFIERS

(U) polypyrrole
radar absorbing material
conducting polymers